Effects of Reversed Austenite on EAC Susceptibility of 17-4PH Stainless Steel in Simulated Geothermal Environment and Its Mechanistic Understanding

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学 位 論 文 題 目	Effects of Reversed Austenite on EAC Susceptibility of 17-4PH Stainless Steel in Simulated Geothermal Environment and Its Mechanistic Understanding（模擬地熱環境における 17-4PH ステンレス鋼の環境助長割れ感受性におよぼす逆変態オーステナイトの影響とその作用機構に関する研究）	
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論文内容要約

Geothermal energy as a renewable energy has three compelling features: zero carbon emissions during operation, higher capacity factor (a measure of the amount of real electric generation time during which a facility is used), and cost effective. Worldwide, it is expected that the demand of geothermal power capacity will have doubled from 2005 to 2020. Regarding the structural trend of the size of geothermal steam turbine blade, it kept almost constant in Japan after 1990s, however, in the global scale, the size continued to increase constantly. It is expected that the blade size will go beyond 36.0 inches for 50 Hz plant, and 32 inches for 60 Hz. This increase of blade size will enhance the output of geothermal unit as well as the efficiency. More importantly, the station cost will reduce by more than 15%, an irresistible incentive to geothermal industry.

The larger size of next generation blade will result in larger centrifugal force on the blade under operation, thus, higher 0.2% proof stress is required. The required stress for next generation blade is higher than current candidate materials, modified 17-4PH and 13Cr. The increased working stress on the longer blade and the increased 0.2% proof stress both exacerbate environmentally assisted cracking (EAC) which is a major failure mechanism for geothermal steam turbine blade. The increased concern over EAC makes it a big challenge for geothermal engineers to increase the 0.2% proof stress of candidate materials. It is extensively accepted that EAC is determined by three factors: stress, material and operating environment. With respect to the factor of material, two parameters are most important: 0.2% proof stress and microstructure. Generally speaking, higher 0.2% proof stress results in higher EAC susceptibility. The working stress is given by design, and the environment is determined by geothermal well properties. Therefore, the most plausible method to address the increased concern over EAC is to enhance the EAC resistance of microstructure.

Modified 17-4PH has proved to be more EAC resistant in H_2S containing geothermal environment than 13Cr, the most widely used geothermal turbine blade material, though its 0.2% proof stress is higher than 13Cr, implying that the microstructure of modified 17-4PH is more resistant to EAC than 13Cr. This modified 17-4PH has been heat treated with a specially designed two-step heat treatment, 1020 ~ 1050°C × 1 h, 825 ~ 845°C × 1 h, 610 ~ 630°C × 3 h. It is believed that this heat treatment gives modified 17-4PH a microstructure with optimal EAC resistance. However, in depth microstructure analysis as well as microstructural correlation with EAC resistance are both in lack. Reversed austenite (RA), reported to appear after two-step tempering at high temperature, is believed to be one microstructure contributing to high EAC resistance because it is well known that austenite could reduce susceptibility to hydrogen embrittlement (HE) which is a conventional concern for 17-4PH. The high EAC resistance microstructure, along with RA, makes modified 17-4PH a promising material to develop a microstructure with adequate EAC resistance for next generation blade. The objective of present research is to clarify the correlation between microstructure of modified 17-4PH and, its mechanical and chemical characteristics. That information will serve as critical basis for next stage microstructure development towards higher EAC resistance.

In chapter 2, the EAC susceptibility of modified 17-4PH in simulated geothermal environment was evaluated by corrosion fatigue tests and compared with that of 13Cr. Before the test, microstructure characterization was performed by metallography and electron backscatter diffraction (EBSD) to provide reliable and fundamental information of modified 17-4PH. It was found that the matrix of modified 17-4PH was lath martensite. Previous research compared the EAC susceptibility between modified 17-4PH and 13Cr in simulated geothermal environment with saturated H_2S, where the predominant EAC mechanism could be hydrogen embrittlement (HE). By contrast, the predominant EAC mechanism in geothermal field without or with little H_2S could be active path corrosion (APC). Different EAC mechanisms very likely resulted in different EAC behaviors. However, no information existed about the EAC behavior of modified 17-4PH in geothermal environment without or with little H_2S. Thus, it was indispensable to evaluate the EAC behavior of modified 17-4PH in that environment, and to compare its EAC resistance with that of 13Cr to confirm that modified 17-4PH was a better candidate than 13Cr. The corrosion fatigue test was performed in a wide range of loading ratio R, from 0 to 0.96, and under various frequencies, from 10 Hz to 0.1 cpm. The specimen used was contoured double cantilever beam specimen, which could maintain constant stress intensity factor when constant load was applied. The quantitative analysis by time domain analysis, a unique way to plot both corrosion fatigue data and stress corrosion cracking (SCC) behavior in one curve, showed that modified17-4PH had similar corrosion fatigue crack growth rate to 13Cr, but lower SCC growth rate than 13Cr though the test temperature was 90°C for modified 17-4PH, and 60°C for 13Cr. This result indicated that modified 17-4PH was a better candidate than 13Cr for next generation blade with larger size. However, the SCC growth rate of modified 17-4PH was above 10^{-7} mm/s, unacceptable for a geothermal power plant usually with life expectancy of over three decades. SEM observation of fracture surface and EBSD analysis of the crack path confirmed the intergranular attack under low loading frequency and high loading ratio. This result suggested the involvement of HE in the EAC behavior. Attention should be paid to the concern that modified 17-4PH would have even higher SCC susceptibility in geothermal environment containing H_2S. A great deal of efforts should be placed upon the microstructure to improve the SCC resistance of modified 17-4PH in geothermal environment.

In chapter 3, microstructural evolution of modified 17-4PH with the two-step tempering mentioned above was analyzed in depth to find out the most promising microstructural factor to address the unacceptable SCC susceptibility. RA and Cu-rich precipitates were believed to be the primary microstructural factors that gave modified 17-4PH a unique microstructure of both higher EAC resistance and of higher 0.2% proof stress than 13Cr. RA and Cu-rich precipitate appeared during the second step tempering of a specially designed two-step tempering for modified 17-4PH. Then the duration of second step tempering was changed to control the volume ratio of RA and Cu-rich precipitation. The various duration of second step tempering was set for 0 h, 0.5 h, 1 h, 2 h, 4h, and 8 h. It was found that, at the beginning two hours, there was a quick increase of the volume ratio of RA, then it showed a tendency of saturation until 8h. The volume ratio of RA peaked at 18% after second step tempering at 620 °C for 2 h. The Cu-rich precipitate did not observed until 2 h, and those formed were identified as BCC structure as did the matrix. Pitting corrosion and mechanical properties, that are most closely linked to SCC susceptibility, were then measured. Pitting test suggested that the RA had little effect on the pitting potential. After pitting test, the surface of all specimens were observed. It was found that intergranular attack (IGA) occurred to all the specimens except for one specimen which did not contain RA because no second step tempering was applied to it. Elemental distribution line scanning by Auger electron spectroscopy showed Ni-peaks ahead of the attacked tips. CalPhad calculation confirmed that RA contained higher Ni than martensite but depleted in Cr. The Ni-peaks and CalPhad calculation indicated that RA caused intergranular attack. Depletion of Cr in RA induced lower corrosion resistance of RA, and subsequently caused preferential corrosion of RA, resulting in IGA. The IGA readily trigger intergranular SCC, albeit, active path corrosion (APC). Meanwhile, the RA had a significant softening effect on the material. The softening effect of RA even dominated the hardening effect of Cu-rich precipitate even though the Cu-rich precipitate was coherent with the matrix. On the other hand, it was believed that RA should reduce HE susceptibility because it had higher hydrogen solubility and slowed down hydrogen diffusion. The complexed effect of RA on SCC and detrimental effect on material strength suggested that RA should be the key to develop a material for next generation blade with high SCC resistance as well as high 0.2% proof stress.

In chapter 4, efforts were made to optimize the microstructure through investigation of the effect of RA on SCC. It should be noted that APC as a mechanism operating on modified 17-4PH in geothermal environment had not yet been confirmed so far. Therefore, the research in this chapter consisted of three parts: investigations of the effect of RA on HE, confirmation of APC, and effect of RA on APC. Two specimens with very similar 0.2% proof stress but different volume ratios of RA were prepared. The two different heat treatments were 1040°C × 3 h, 835°C × 1 h, and 620°C × 1 h, marked ST1, and 1040°C × 3 h, 835°C × 1 h, 650°C × 4 h, marked ST650. The volume ratios of RA were 16.5% and 1.5%, respectively. With respect of the effect on HE, hydrogen pre-charged ST1 after slow strain rate testing (SSRT) in high vacuum showed brittle quasi-cleavage, while ST650 did ductile transgranular crack, strongly suggesting the detrimental effect of RA on HE. The reduction of residual compressive strain in martensite was observed in ST1 by comparing residual strain in martensite and RA through X - ray diffraction measurement. This result was caused by RA. The relaxation of compressive strain might promote HE. The SSRT under cathodic polarization caused larger reduction of strain ratio to ST1 than ST650, further confirming the detrimental effect of RA on HE. After the SSRT under cathodic polarization, the side surface just below the fracture surface of ST1 was analyzed by EBSD. It was found that almost all the RA transformed to martensite during loading process. It is well known that austenite has much solubility of hydrogen than martensite. The phase analysis by EBSD indicated that the underlying mechanism of detrimental effect of RA on HE was the hydrogen release from RA when RA transformed to martensite due to plastic deformation caused by load above elastic limit. Regarding confirmation of APC, SSRT under anodic polarization of specimen ST1 was performed. It was found that its strain ratio reduced with higher anodic polarization, and pit-initiated intergranular crack was also observed, in contrast to the ductile transgranular crack of the specimen without anodic polarization. These results confirmed the involvement of APC in the EAC susceptibility of modified 17-4PH. With respect to the effect of RA on APC, same anodic polarization of 20 $\mu A/cm^2$ caused a larger reduction of strain ratio to ST1 than to ST650. Pit-initiated intergranular crack was found on ST1, while ST4 showed only ductile fracture. Those results indicated the harmful effect on APC. The detrimental effect of RA on APC was within expectation since RA in grain boundary area was preferentially corroded, resulting in intergranular SCC. Surprisingly, RA presented harmful effect on HE, contradictory to what people believed that RA would be beneficial to HE.

Proposal was also made for next stage development of modified 17-4PH. In order to improve the EAC resistance, the volume ratio of RA was sincerely suggested to reduce. Ni, a well-known strong austenite stabilizer, then was recommended to reduce. Addition of Mo is effective for enhancing pitting resistance. Then, the pit-initiated intergranular attack would be alleviated, thus, improving the EAC resistance. As regards improvement of mechanical properties, Cu concentration should be decreased to decrease the size of Cu-rich precipitate, and thus, to increase the 0.2% proof stress.